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Chemical Physics Letters 375 (2003) 666–669

CHEMICAL PHYSICS LETTERS

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A simple model for thermal conductivity of carbon nanotube-based composites

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Received 16 March 2003; in final form 30 May 2003

Abstract

A quite simple formula for the thermal conductivity enhancement in carbon nanotube composites is presented based on a conventional model. This simple formula predicts much higher thermal conductivity enhancement even in the dilute case of the carbon nanotubes, due to ultrahigh thermal conductivity and aspect ratio of the carbon nanotubes. By applying this model to nanotube suspensions recently reported in the literature, we show that the conventional model is still valid for the nanotube-based composites.

Carbon nanotubes have been intensively studied because of their unique physical properties and many potential applications, including nanoprobes, field electron emitters, nanotweezers, nanobearings, and so forth (see, for example, a recent review [1]). Among these applications the development of nanocomposites based on the carbon nanotubes is a promising direction in nanotechnology, in which the carbon nanotubes are used as novel fillers to employ their unique physical properties. For example, carbon nanotubes are used to reinforce polymers [2–5], since the carbon nanotubes are much stronger and have larger aspect ratio than conventional carbon fibers. But progress in the mechanical composites has proved difficult due mainly to weak nanotube/matrix bonding. Alternatively, the carbon nanotubes have recently been embedded into polymers or other media to get materials with good electrical and thermal transport properties [6–8]. Very recent studies have shown that the thermal conductivity of the carbon nanotube composites can be greatly enhanced [7,8], since the carbon nanotubes have unusually high thermal conductivity [9,10]. Of interesting to note is an *anomalous* thermal conductivity enhancement observed in carbon nanotube suspensions in which homogeneous dispersion of the carbon nanotubes can be more easily achieved than in solid composites. The *anomalous* thermal conductivity enhancement is theoretically intriguing because the measured thermal conductivities have been considered to be

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doi:10.1016/S0009-2614(03)00956-4

greatly higher than predicted from existing theories [8]. A complete theoretical analysis of the thermal transport behavior of these carbon nanotube media is still missing. In this Letter, we present understanding of the anomalous thermal behavior of the nanotube media, based on a conventional model.

In analyzing the thermal transport behavior in heterogeneous media, various effective medium approaches (EMA) like the Maxwell–Garnett (MG) approximation have been used to determine the effective thermal conductivity of different composite structures [11,12]. The validity of the conventional EMA has been proved, and the MG-EMA has been known to be reasonable for matrix-based composites with small filling ratios. Our idea is to develop the EMA formula able to describe carbon nanotube media and compare these results with recent experiments, studying the range of validity of the conventional theory for carbon nanotube-based materials.

First we briefly review the multiple-scattering approach following Nan [11]. Let us consider a composite medium whose local thermal conductivity varies from point to point. The variation can be expressed in the form: $K(r) = K^0 + K'(r)$, where K^0 denotes a constant part of a homogeneous medium and $K'(r)$ is an arbitrary fluctuating part. By using the Green function G for the homogeneous medium defined by K^0 and the transition matrix T for the entire composite medium, a rigorous solution for the temperature gradient distribution can be obtained. The resultant effective thermal conductivity K_e of the composite is expressed as

$$K_e = K^0 + \langle T \rangle (I + \langle GT \rangle)^{-1}, \tag{1}$$

where I is the unit tensor and $\langle\,\rangle$ denotes spatial averaging. The matrix, T, is

$$T = \sum_n T_n + \sum_{n,m \neq n} T_n G T_m + \cdots, \tag{2}$$

where the first term is the sum of the T matrices of n particles and the successive terms represent the interaction between particles. An accurate calculation of T is a formidable problem. For simplicity of calculation, T is generally approximated as

$$T \cong \sum_n T_n = \sum_n K'_n (I - GK'_n)^{-1}, \tag{3}$$

thereby neglecting interparticle multiple scattering. Obviously, this approximation is valid when the inclusion particles are dispersed in the matrix.

Now consider a carbon nanotube-based composite with carbon nanotubes randomly dispersed in a matrix. The nanotube/matrix interface is assumed to be effective for the transport of energy across it. Let us take the matrix phase as the homogeneous reference medium, i.e., $K^0 = K_m$, K_m being the thermal conductivity of the matrix. This leads to a MG type EMA of the theory, i.e.,

$$\frac{K_e}{K_m} = \frac{3 + 2f[\beta_x(1 - L_x) + \beta_z(1 - L_z)]}{3 - f(2\beta_x L_x + \beta_z L_z)}, \tag{4}$$

$$\beta_x = \frac{K_x - K_m}{K_m + L_x(K_c - K_m)}, \quad \beta_z = \frac{K_z - K_m}{K_m + L_z(K_c - K_m)}, \tag{5}$$

here K_x and K_z are the thermal conductivities of the carbon nanotubes along transverse and longitudinal axes, respectively; f is the volume fraction of the nanotubes; and L_x and L_z are well-known geometrical factors dependent on the nanotube aspect ratio p and given by

$$L_x = \frac{p^2}{2(p^2 - 1)} - \frac{p}{2(p^2 - 1)^{3/2}} \cosh^{-1} p, \quad L_z = 1 - 2L_x. \tag{6}$$

High p of over 100 for the carbon nanotubes gives $L_x = 0.5$ and $L_z = 0$. Thus the MG-EMA (4) reduces to

$$\frac{K_e}{K_m} = \frac{3(K_x/K_m + 1) + f[2(K_x/K_m - 1) + (K_x/K_m + 1)(K_z/K_m - 1)]}{3(K_x/K_m + 1) - 2f(K_x/K_m - 1)}. \tag{7}$$

For the carbon nanotubes, either single-walled or multi-walled, the thermal conductivity is quite high, e.g., from 600 to 6000 W/mK [9,10]. If K_x and K_z of the carbon nanotubes are much larger K_m, then one get a simple equation as follows:

$$\frac{K_e}{K_m} = \frac{3 + fK_c/K_m}{3 - 2f}, \tag{8}$$

where K_c is the thermal conductivity of the carbon nanotubes. Furthermore, in the dilute limit as in the carbon nanotube composites reported in the literature, e.g., $f < 0.02$, the thermal conductivity enhancement is simply given by

$$\frac{K_e}{K_m} = 1 + \frac{fK_c}{3K_m}. \tag{9}$$

Even in the case of K_x being lower K_z [i.e., high anisotropy in the thermal conductivity of the carbon (multi-walled) nanotubes] but $K_z/K_m \gg 1$, the dilute Eq. (9) still holds. Actually, only one isotropic thermal conductivity K_c was observed for the carbon nanotubes. This quite simple relation (9) clearly demonstrates the large thermal conductivity enhancement induced by the high thermal conductivity of the carbon nanotubes.

For illustration, Fig. 1 shows a comparison between Eq. (9) and a recent experiment on nanotube suspensions [8]. As seen, the simple equation derived from the conventional model predicts high thermal conductivity enhancement as observed in experimental [8] or even higher enhancement than experimental results. Thus the thermal conductivity enhancement in the composites with dilute carbon nanotubes is not *anomalously* beyond theoretical predictions. That the thermal conductivity of the nanotube suspensions is *anomalously* greater than those theoretical predictions [8] is because those models used in [8] might not be valid for the carbon nanotube-based composites. For instance, the MG dilute formula used in [8] is

$$\frac{K_e}{K_m} = 1 + 3f, \tag{10}$$

which is valid only for nearly spherical particles ($p \approx 1$), but not for nanotubes ($p \gg 1$).

The simple MG-EMA\model for the nanotubes is valid for the matrix-based composites in which nanotubes are surrounded by the matrix. For this type of matrix-based composite, the validity of the MG-EMA formula derived above is for very low range of the volume fraction of the carbon nanotubes. If there are continuous nanotubes networks in the composite (e.g., above its percolation threshold), the MG-EMA would underestimate the effective thermal conductivity of the nanotube composite. This is especially so for the larger differences in thermal conductivities of the matrix and nanotubes (e.g., $K_c/K_m > 100$), as in the present carbon nanotube composites.

On the other hand, however, Eq. (8) or (9) predicts higher thermal conductivity values than the experimental observations so far, as shown in Fig. 1. This implies that there is still much room for further enhancement in the thermal conductivity of the carbon nanotube-based materials by improvement of processing and quality of carbon nanotubes used. The large discrepancies between the predictions and current experiments could be due to interfacial thermal resistance between the matrix and nanotubes, and aggregation and twist of the nanotubes in the composites. The nanotube/matrix interfacial thermal contact resistance can arise from the combination of a poor mechanical or chemical adherence at the interface and other mismatch, and the presence of the nanotube/matrix interfacial thermal resistance could result in a drop in the effective thermal conductivity. The aggregation of the nanotubes could lead to a decrease in K_c [13], and the twist of the nanotubes could lead to a decrease in effective aspect ratio values of the nanotubes. The lower enhancement in the effective thermal conductivity of the nanotube composites than predicted could also reflect

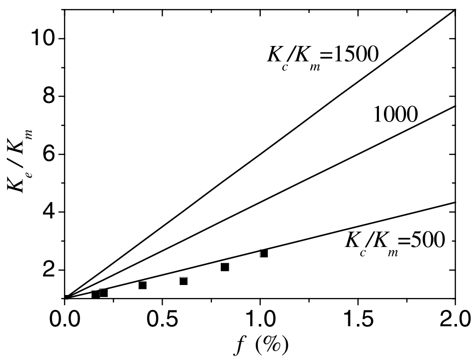

Fig. 1. The thermal conductivity enhancement in the carbon nanotube-based composites in the dilute case of dispersion of a very small amount of nanotubes. Solid lines are predicted by using Eq. (9) for three ratios of K_c/K_m. For comparison, the recent experimental results for the nanotube suspensions [8] (solid dots) are also shown.

processing challenges and poor nanotube dispersion, especially in solid composites. As in the mechanical composites [2–5], the thermal conductivity enhancement in the nanotube-based composites is still below the expected, which could be mainly limited by processing.

In summary, a quite simple equation for predicting the effective thermal conductivity of the nanotube-based composites has been given based on the conventional effective medium model. The theory shows that dispersion of a quite small amount of carbon nanotubes can result in a remarkable enhancement in the effective thermal conductivity of the composites. Comparison with recently reported experiment for the nanotube suspensions illustrates that the observed *anomalous* thermal conductivity enhancement lies within reasonable range covered by the conventional model rather than really *anomalously* beyond the conventional model. The reasonable conventional models are still valid for the carbon nanotube-based composites.

Acknowledgements

This work was supported by the Ministry of Sciences and Technology of China through 973-Project (Grant No. G2000067108 and 2002CB613303) and the NSF of China.

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